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XIX.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

THE β PHENYLTRIBROMPROPIONIC ACID.

By Leonard P. Kinnicutt and George M. Palmer.

Presented May 9th, 1883.

The α phenyltribrompropionic acid and the products formed when this acid is decomposed by boiling water were briefly described by one of us last year.* During the past winter the study of the β acid was undertaken, and it has been considered best to give at this time the results so far obtained, as the further investigation must be carried on in different relations.

The β phenyltribrompropionic acid was obtained by the action of dry bromine on β monobromcinnamic acid, this last having been prepared in the way previously described.†

By the action of bromine on β monobromcinnamic acid, Glaser‡ obtained an acid, which he describes as melting during the absorption of the bromine and only solidifying again after several days. The melting point he found to be 45–48° C. The results obtained by us are very different. Perfectly pure β monobromcinnamic acid melting at 120° C. was placed under a bell glass with the theoretical amount of bromine. Not the slightest indication of melting was observed, and after twenty-four hours the bromine was all absorbed. The acid so obtained was purified by crystallization from chloroform and melted at 151° C. It is soluble in alcohol, ether, carbonic disulphide, chloroform, and benzol.

The analyses gave the following results: —

1. 0.2711 gr. substance gave 0.2788 gr. CO_2 and 0.0454 gr. H_2O.
2. 0.3845 gr. substance gave 0.3912 gr. CO_2 and 0.0702 gr. H_2O.
3. 0.1894 gr. substance gave 9.2769 gr. AgBr.
4. 0.1839 gr. substance gave 0.2696 gr. AgBr.

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* Kinnicutt, Amer. Chem. Jour., iii. 4.

† Ibid.

‡ Annalen der Chemie, cxliii. 339.

Calculated for $C_9H_7Br_3O_2$.		Found. 1.	2.	3.	4.
C	27.9	28.04	27.73		
H	1.8	1.86	2.00		
Br	62.17			62.24	62.40

Decomposition of the β Phenyltribrompropionic Acid by Water heated to 100° C.

Twenty grammes of the acid were placed in a flask with two hundred cubic centimeters of boiling water. Decomposition began immediately, a volatile oil separating out, which at the end of eight hours had for the greater part been carried over with the steam, leaving a clear liquid that on cooling deposited a white crystalline substance. On examination, the oil was found to be a dibromstyrol, the white crystalline substance the *a* monobromcinnamic acid, and a third substance, which remained in solution in the liquid, gave on analysis results corresponding very closely to those required for a phenyldibromlactic acid.

Dibromstyrol, $C_8H_6Br_2$.

The oil that was carried over by the steam was separated from the water by ether, and, after thorough washing to remove all traces of hydrobromic acid, the ether was distilled off. The oil thus obtained was of a light amber color, growing gradually darker, and giving off on long standing traces of hydrobromic acid.

It boils at 253–254° C. with slight decomposition, hydrobromic acid being formed.

The analyses of the oil, dried over sulphuric acid, gave the following results: —

1. 0.2518 gr. substance gave 0.3328 gr. CO_2 and 0.0518 gr. H_2O.
2. 0.3592 gr. substance gave 0.4810 gr. CO_2 and 0.0744 gr. H_2O.
3. 0.2518 gr. substance gave 0.3615 gr. AgBr.
4. 0.3032 gr. substance gave 0.4379 gr. AgBr.

Calculated for $C_8H_6Br_2$.		Found. 1.	2.	3.	4.
C	36.64	36.02	36.50		
H	2.29	2.26	2.30		
Br	61.06			61.10	61.40

The properties of this oil correspond in all respects with those of the dibromstyrol obtained from the decomposition of the *a* phenyltribrompropionic acid,* and it seems most probable that the two substances are not simply isomeric, but identical. This point, however, cannot be positively settled till a careful study has been made of the addition products of both compounds.

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* Kinnicutt, Amer. Chem. Jour., iii. 4.

a Monobromcinnamic Acid.

The nearly clear liquid from which the bromstyrol had been distilled was made slightly alkaline with sodic carbonate, and shaken with ether to remove the last traces of the oil. The solution was then evaporated to a volume of about one hundred cubic centimeters and acidified with dilute hydrochloric acid. A white precipitate was thrown down, which after one crystallization from boiling water melted at 132° C., and proved to be the *a* monobromcinnamic acid.

Two bromine determinations gave the following results: —

1. 0.1986 gr. substance gave 0.1661 gr. AgBr.
2. 0.2242 gr. substance gave 0.1874 gr. AgBr.

Calculated for $C_9H_7BrO_2$.		Found. 1.	2.
Br	35.25	35.58	35.56

The barium salt, formed by adding baric chloride to a dilute solution of the acid in warm water, resembled in every respect the barium salt of *a* monobromcinnamic acid as described by Glaser.* It was only slightly soluble in cold water and insoluble in alcohol. The barium salt of the *β* bromcinnamic acid is hygroscopic, and soluble in alcohol.

The salt gave on analysis the following result: —

0.3092 gr. substance gave 0.1233 gr. $BaSO_4$.

Calculated for $(C_9H_6BrO_2)_2Ba$.		Found.
Ba	23.23	23.42

The formation of the *a* monobromcinnamic acid from both the *a* and *β* phenyltribrompropionic acids was rather to be expected, as Glaser has found that the *β* monobromcinnamic acid is changed into the *a* by distillation, or by heating it with hydriodic acid,† and, moreover, Barish has shown that from both the *a* and *β* acids only the ethyl ether of the *a* acid can be obtained.‡

In speaking of these acids we have used the nomenclature proposed by Glaser. For although it is very probable that his *a* acid is in fact the β, it does not seem desirable to change names that have become familiar until it is absolutely necessary; and notwithstanding the work that has been done in the investigation of these acids during the past five years, no direct proof has been given as to the position of the bromine atoms.

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* Annalen der Chemie, cxliii. 334.

† Ibid., 336.

‡ Jour. fur Prakt. Chemie, cxxviii. 185.

Phenyldibromlactic Acid.

On evaporating the filtrate from the α monobromlactic acid to a small volume, a substance crystallized out that melted at about 180° C. After recrystallization several times from water, the melting point rose to 184° C., and it gave on analysis amounts of carbon, hydrogen, and bromine corresponding to those required for a phenyldibromlactic acid.

The acid is very soluble in water, alcohol, and ether, soluble in chloroform, and slightly soluble in carbonic disulphide and benzol.

We have not as yet succeeded in obtaining the acid in large enough qnantities to study its salts, or to decide which of the several possible formulas correctly represents its structure.

The analyses gave the following results: —

1. 0.1854 gr. substance gave 0.2257 gr. CO_2 and 0.0440 gr. H_2O.
2. 0.1989 gr. substance gave 0.2440 gr. CO_2 and 0.0470 gr. H_2O.
3. 0.1605 gr. substance gave 0.1870 gr. AgBr.
4. 0.1812 gr. substance gave 0.2122 gr. AgBr.

Calculated for $C_9H_8Br_2O_3$.		Found.			
		1.	2.	3.	4.
C	33.34	33.21	33.42		
H	2.46	2.63	2.62		
Br	49.37			49.60	49.70

Action of Bromine on Dibromstyrol.

The dibromstyrol obtained from the decomposition of the β phenyltribrompropionic acid was placed under a bell glass, with an excess of bromine. The oil gradually thickened, and after two days had absorbed about its own weight of bromine. It was then placed over quicklime, and after remaining there three or four days was washed thoroughly with water, and then separated from the water by shaking with ether. The so purified oil gave on analyses the following amounts of bromine: —

1. 0.2050 gr. substance gave 0.3646 gr. AgBr.
2. 0.2110 gr. substance gave 0.3737 gr. AgBr.
3. 0.2055 gr. substance gave 0.3651 gr. AgBr.

Calculated for $C_8H_6Br_4$.		Found. 1.	Found. 2.	Found. 3.
Br	75.82	75.68	75.34	75.60

The substance is evidently a tetrabromstyrol. It is a thick viscous oil, soluble in alcohol, ether, and carbonic disulphide. It begins to decompose on heating at a comparatively low temperature.

It is to be hoped that the study of the products formed by the action of boiling water or dilute alkalies on the above compound, and also on the substance obtained by the addition of bromine to the dibromstyrol formed from the *α* phenyltribrompropionic acid, will show not only the structure of the two dibromstyrols, but also of the two monobromcinnamic acids.